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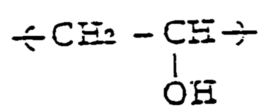
(71) Applicant: KURARAY CO., LTD.
1621 Sakazu
Kurashiki-City(JP)

(72) Inventor: Kamachi, Mikiharu
2-11-5, Midorigaoka
Toyonaka-city, Osaka(JP)
Inventor: Yamamoto, Tohei
1364-611, Goji, Yumesaki-cho
Shikama-gun, Hyogo(JP)
Inventor: Sato, Toshiaki
2045-1, Sakazu
Kurashiki-city, Okayama(JP)
Inventor: Fukunishi, Yoshiharu
2045-1, Sakazu
Kurashiki-city, Okayama(JP)

(74) Representative: Vossius & Partner
Siebertstrasse 4 P.O. Box 86 07 67
D-8000 München 86(DE)

(54) Vinyl alcohol polymers and a process for their production.

(57) The present invention provides vinyl alcohol polymers containing the unit (I) and the unit (II) represented by the following formulae, having a content of the unit (I) from 10 to 99.99 mol% and a content of the unit (II) from 90 to 0.01 mol%, a diad syndiotacticity of not less than 55 mol% and an intrinsic viscosity of polyvinyl acetate btained by acetylation of 0.7 dl/g, which is measured in benzene at 30° C.



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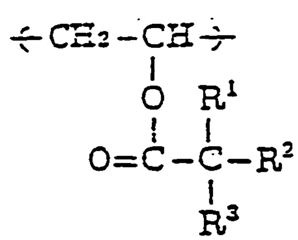

(II)

wherein R^1 is a hydrogen atom or a hydrocarbon group, and each of R^2 and R^3 is a hydrocarbon group.

Also provided is a process for producing vinyl alcohol polymers which comprises hydrolyzing, in the substantial absence of oxygen or in the presence of an antioxidant, homopolymers or copolymers of a vinyl ester represented by the following formula (III):

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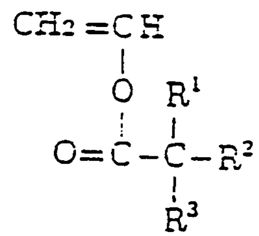


(III)

wherein R^1, R^2 and R^3 are the same as defined above; the above vinyl alcohol polymers comprising a vinyl alcohol unit represented by the formula (I) and a vinyl ester unit represented by the formula (II).

Further provided are films and gels, comprising vinyl alcohol polymers having a syndiotacticity of not less than 55 mol%, which are excellent in water resistance, heat resistance, wet heat resistance, and durability.

Still further provided is a process for producing shaped articles comprising vinyl alcohol polymers which comprises contacting a solution comprising vinyl alcohol polymers having a syndiotacticity of not less than 55 mol% with an aqueous solution containing an organic solvent in an amount of less than 50 wt%.

VINYL ALCOHOL POLYMERS AND A PROCESS FOR THEIR PRODUCTION

The present invention relates to vinyl alcohol polymers and a process for their production. In particular, it relates to vinyl alcohol polymers having a high syndiotacticity and a high degree of polymerization which contain vinyl alcohol units and vinyl ester units, and also to a process for their production.

Polyvinyl alcohols,i.e. the hydrolyzed products of polyvinyl acetate belong to the few crystalline water-soluble polymers. They have excellent interfacial characteristics and mechanical properties, which render them useful as agents for paper processing, stabilizers for emulsions and the like. In addition, they are used as raw materials for polyvinyl alcohol films and the like. Recently, the use thereof in new fields such as raw materials for gels have been developed.

Polyvinyl alcohols commercially available are stereochemically "atactic" and have a diad syndiotacticity of about 53 mol%. As is commonly known, a polyvinyl alcohol with an excellent stereoregularity has physical properties significantly different from those of atactic polymers due to hydrogen bonds. Especially polyvinyl alcohols having a diad syndiotacticity of at least 55 mol% become easy to crystallize, which can increase the usefulness of the polyvinyl alcohols. Several processes are proposed for the production of polyvinyl alcohols with a high syndiotacticity, among which a process comprising the hydrolysis of polyvinyl pivalate can be mentioned. For example, Sakaguchi et al. describe a polyvinyl alcohol obtained by hydrolyzing polyvinyl pivalate in a mixed solvent of acetone and water in the presence of potassium hydroxide (cf. Kobunshi Kagaku, 27, 758-762 (1970)). Nozakura et al. reported that a polyvinyl alcohol was obtained by hydrolyzing polyvinyl pivalate in a mixed solvent of either acetone and methanol or dioxane and methanol, followed by the hydrolysis thereof in methanol in the presence of potassium hydroxide (cf. Journal of Polymer Science Polymer Chemistry Edition, 11, 279-288 (1973)). Furthermore, Imai et al. reported that a polyvinyl alcohol was obtained by hydrolyzing polyvinyl pivalate in acetone and then in dimethyl sulfoxide in the presence of potassium hydroxide (cf. Journal of Polymer Science Polymer Chemistry Edition, 26, 1961-1968 (1988)).

However, in general, due to steric hindrance polyvinyl esters having bulky side chains as polyvinyl pivalate are difficult to hydrolize. Therefore, highly hydrolyzed polyvinyl alcohols cannot be obtained under the conditions applied conventionally to polyvinyl acetates. For example, according to the above-mentioned paper of Sakaguchi et al., the degree of hydrolysis of the obtained polyvinyl alcohol is confined below about 52%. The degree of hydrolysis and the degree of polymerization of the polyvinyl alcohol obtained according to the above-mentioned paper of Nozakura et al. are unknown. Therefore, the present inventors made supplementary tests and found that the polyvinyl pivalate was hydrolyzed to a polyvinyl alcohol having a rather high degree of hydrolysis, which colored dark brown and degraded. Moreover, this process is troublesome to conduct due to the need of repeated hydrolysis. The polyvinyl alcohol obtained according to the process of Imai et al. had a low degree of polymerization, which suggests that the degree of polymerization had decreased during the hydrolysis. Due to the two-stage hydrolysis, the process reported by Imai et al. is also troublesome to conduct.

An object of the present invention is to provide novel vinyl alcohol polymers having a high syndiotacticity and a high degree of polymerization.

Another object of the present invention is to provide a process for producing vinyl alcohol polymers having a high syndiotacticity and a high degree of polymerization while preventing the degree of polymerization from decreasing during hydrolysis.

A further object of the present invention is to provide vinyl alcohol polymer films, obtained from the above vinyl alcohol polymer, having a high syndiotacticity and a high degree of polymerization, with the films being excellent in strength, heat resistance, water resistance, wet heat resistance, and durability.

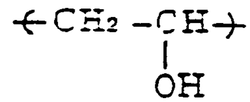
A still further object of the present invention is to provide gels comprising the above vinyl alcohol polymers, which are excellent in water resistance, heat resistance, durability and strength.

Preferably, the present invention provides vinyl alcohol polymers having vinyl alcohol units from 10 to 99.99 mol%, vinyl pivalate units from 90 to 0.01 mol%, a syndiotacticity of not less than 55 mol% and an intrinsic viscosity of polyvinyl acetate obtained by acetylation of not less than 0.70 dl/g which is measured in b nzene at 30 °C.

Preferably, th present invention provid s a process for producing vinyl alcohol polymers without decreasing the degree of polymerization during hydrolysis in the substantial absence of oxygen or in the presence of an antioxidant.

The present invention provides vinyl alcohol polymers containing a unit (I) and a unit (II) represented by the following formulae, having a content of the unit (I) from 10 to 99.99 mol% and a content of the unit (II) from 90 to 0.01 mol%, a diad syndiotacticity of not less than 55 mol% and an intrinsic viscosity of polyvinyl

acetate obtained by acetylation of 0.7 dl/g, which is measured in benzene at 30° C.



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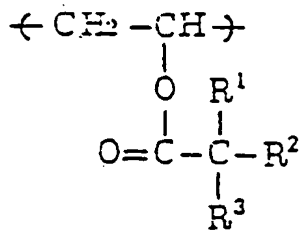


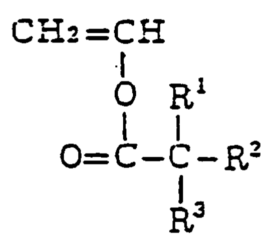
(II)

wherein R^1 is a hydrogen atom or a hydrocarbon group and each of R^2 and R^3 is a hydrocarbon group.

The above polymers contain as essential units vinyl alcohol units represented by the formula (I) and vinyl ester units represented by the formula (II), the content of vinyl alcohol unit (I) being from 10 to 99.99 mol% and the content of vinyl ester unit (II) being from 90 to 0.01 mol%. The content of vinyl alcohol units is not more than 99.99 mol% because polymers containing vinyl alcohol units of more than 99.99 mol% are extremely difficult to be industrially produced. On the other hand, polymers containing vinyl alcohol units of less than 10 mol% may not have enough intermolecular force which is one of the characteristics thereof.

The content of vinyl alcohol unit of the polymer is appropriately selected according to their use. Polymers having vinyl alcohol units from 10 to 55 mol% are mainly used for applications where low crystallinity is preferred. On the other hand, the polymers having vinyl alcohol units from 55 to 99.99 mol%, preferably 90 to 99.99 mol%, are mainly used for applications where high crystallinity is preferred. And the polymers having vinyl alcohol units from 96 to 99.99 mol%, preferably from 97 to 99.99 mol%, are very suitable for the above applications.

Preferred examples of hydrocarbon groups represented by R^1, R^2 and R^3 in the general formula (II) are ones having 1 to 18 carbon atoms such as lower alkyl groups, e.g.,a methyl, ethyl, propyl and butyl group; aryl groups, e.g., a phenyl group; and cycloalkyl groups, e.g., a cyclohexyl group. Preferably each of R^1, R^2 and R^3 is a methyl group in view of the general-purpose usefulness of the vinyl ester represented by the following formula (III) which corresponds to the vinyl-ester-unit-donating monomer :



(III)

wherein R^1, R^2 and R^3 are as defined above.

Vinyl alcohol polymers of the present invention have a content of vinyl alcohol units from 10 to 99.99 mol% and a content of vinyl ester units from 90 to 0.01 mol% and may further contain ethylene units which may be substituted. Examples of monomers which correspond to these optionally substituted ethylene units are vinyl esters except the vinyl esters represented by the formula (III), such as vinyl formate, vinyl acetate, vinyl propionate, vinyl valerate, vinyl caprate and vinyl laurate; olefins, such as ethylene, propylene, isobutylene, α -octene, α -dodecene and α -octadecene; α ,β -unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic anhydride and itaconic acid, or salts, monoalkyl esters or dialkyl esters thereof; α ,β -unsaturated nitril s, such as acrylonitrile and methacrylonitrile; unsaturat d amides, such as acrylic amide, methacrylic amide and N-vinylpyrrolidone; lefinsulfonic acids, such as ethylenesulfonic acid, allylsulfonic acid and m thallylsulfonic acid, or salts th reof; alkyl vinyl ethers such as isopropyl vinyl ether; polyoxyalkylene alkylallyl ethers such as polyoxy thyl ne methyl allyl eth r; alkyl allyl

ethers such as isopropyl allyl ether; saturated allyl carboxylate esters such as allyl acetate; vinyl ketones such as methyl vinyl ketone; halogenated olefins such as vinyl chloride and vinylidene chloride; and monomers containing amino groups or quaternary ammonium groups, such as 1-vinyl-2-methyl imidazole and 1-vinyl-2,3-dimethyl imidazolinium chloride. The content of these ethylene units which may be substituted is generally not more than 5 mol%.

In the present invention, the degree of polymerization of the vinyl alcohol polymers is expressed by the value of the intrinsic viscosity, $[\eta]$ of the vinyl acetate polymer obtained by the acetylation thereof measured in benzene at 30°C. The intrinsic viscosity of the vinyl acetate polymers of the present invention, measured by the above method, is not less than 0.70 dl/g, preferably not less than 1.0 dl/g, more preferably not less than 1.5 dl/g, most preferably not less than 2.0 dl/g and particularly not less than 2.5 dl/g.

In this case the gels prepared from the vinyl alcohol polymers have a high mechanical strength. However, the upper limit of the above-described intrinsic viscosity of the vinyl alcohol polymers is preferably 15.0 dl/g since their processability becomes difficult in case that the intrinsic viscosity is too high.

The diad syndiotacticity of the vinyl alcohol polymers of the present invention is not less than 55 mol%, preferably not less than 57 mol%. In case that the diad syndiotacticity is not less than 55 mol%, the above polymers are easy to crystallize and are hence capable of forming gels with a high melting point.

The diad syndiotacticity (s) is calculated from the triad syndiotacticity determined by the proton NMR spectrometry of the vinyl alcohol polymers dissolved in d_6-DMSO (cf. T. Moritani et al., Macromolecules, 5, 577 (1972)). (S) means syndiotacticity, (H) heterotacticity and (I) means isotacticity as:

s = S + H/2 (diad syndiotacticity)

i = I + H/2 (diad isotacticity).

Vinyl alcohol polymers of the present invention having a 1,2-glycol content of 1.8 to 5 mol% are excellent in solubility and processability.

In the substantial absence of oxygen or in the presence of an antioxidant, the vinyl alcohol polymers of the present invention containing vinyl alcohol units represented by the formula (I) and a vinyl ester units represented by the general formula (II) can be produced by the hydrolysis of homopolymers or copolymers of vinyl esters represented by the formula (III), without a significant decrease in the degree of polymerization during the hydrolysis.

Hereinafter, the process for producing the vinyl alcohol polymers of the present invention is described in more detail.

In the formula (III) representing the vinyl esters used in the process of the present invention, preferred examples of the hydrocarbon groups represented by R^1, R^2 and R^3 are hydrocarbon groups having 1 to 18 carbon atoms, e.g., lower alkyl groups such as methyl, ethyl, propyl and butyl groups; aryl groups such as a phenyl group; and cycloalkyl groups such as a cyclohexyl group. Each of R^1, R^2 and R^3 is preferably a methyl group in view of the availability of the vinyl ester. Namely, the most preferred vinyl ester is vinyl pivalate and vinyl versatate is also used. There are two types of the comonomers capable of forming the copolymer of the vinyl esters represented by the general formula (III). The first type of comonomers are those which generate vinyl alcohol units by hydrolysis and the second type of comonomers are those except the first type. The first type of comonomers is used to control the tacticity and the second type is used to change the properties of vinyl alcohol polymers. Examples of the former type are vinyl esters such as: vinyl acetate, vinyl formate, vinyl propionate, vinyl valerate, vinyl pivalate, vinyl versatate, vinyl laurate, vinyl stearate, and vinyl benzoate.

Examples of the latter type are olefins such as ethylene, propylene, 1-butene and isobutene;

acrylic acid and its salts; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, i-propyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, and octadecyl acrylate; methacrylic acid and its salts; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, i-propyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, and octadecyl methacrylate; acrylamide, N-methylacrylamide, N-ethylacrylamide, N,N-dimethylacrylamide, diacetoneacrylamide, and acrylamide propanesulfonic acid and its salts; acrylamide propyldimethylamine and its salts and quarternary salts; methacrylamide derivatives such as N-methylolacrylamide and its derivatives; vinyl thers such as methyl vinyl ther, ethyl vinyl ther, n-propyl vinyl ether, i-propyl vinyl eth r, n-butyl vinyl ether, i-butyl vinyl ether, t-butyl vinyl ether, dodecyl vinyl ether, and stearyl vinyl ether; nitriles such as acrylonitrile and methacrylonitrile; vinyl halides such as vinyl chloride , vinylidene chloride, vinyl fluoride, and vinylidene fluoride; allylic compounds such as allyl acetate and allyl chloride; maleic acid and its salts and esters; itaconic acid and its salts and esters; vinyl silyl compounds such as vinyltrimethoxysilane; isopropenyl acetate and the like. In order to obtain the above-described highly syndiotactic vinyl alcohol polymers, th

polymers to be subjected to the hydrolysis are preferably homopolymers represented by the formula (III) or copolymers obtained by the copolymerization of the vinyl esters represented by the formula (III) with comonomers in a ratio to the total of monomer of generally not less than 55 mol% though depending upon the type of the comonomer used. The homopolymers and copolymers of the vinyl esters represented by the formula (III) are produced by the homopolymerization of the above vinyl esters or the copolymerization of the above vinyl esters with comonomers according to a conventional process such as bulk polymerization, solution polymerization, suspension polymerization, or emulsion polymerization.

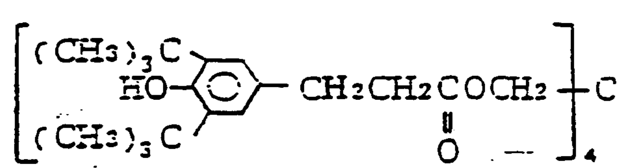
There is no limitation concerning the polymerization temperature of the vinyl esters. Appropriately it is selected in the range of from -80° to 300° C. In case that the polymerization temperature is in the range of from 70° to 200° C, the polyvinyl alcohol polymers obtained have a 1,2-glycol content of not less than 1.8 mol% and a syndiotacticity of not less than 55 mol%. At a polymerization temperature below 70° C, the 1,2-glycol content is less than 1.8 mol%. Furthermore, at a polymerization temperature exceeding 300° C, the syndiotacticity is less than 55 mol%. The 1,2-glycol content can be controlled by the copolymerization of vinylene carbonate.

The hydrolysis according to the present invention is performed in the presence of an alkali. Either ester exchange reaction or direct hydrolysis reaction can be selected, depending upon the amount of the alkali used or the kind of solvent used. Examples of the alkali are alkali metal hydroxides such as potassium hydroxide, sodium hydroxide and lithium hydroxide; and alkali metal alcoholates such as sodium methoxide, sodium ethoxide, potassium methoxide, potassium ethoxide and potassium t-butoxide. By using these alkalis, hydrolysis is performed as follows. In the substantial absence of oxygen or in the presence of an antioxidant, the homopolymers or copolymers of the vinyl esters represented by the formula (III) are hydrolyzed with the above-described alkalis in a solvent capable of dissolving or fully swelling the homopolymers or copolymers.

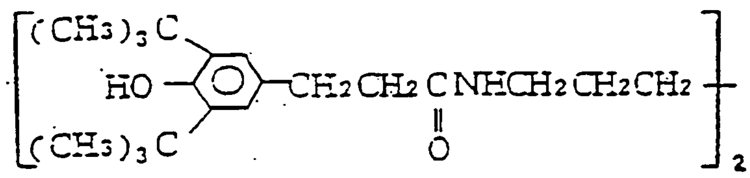
Any solvent can be used for the hydrolysis as long as it can dissolve or swell the homopolymers or copolymers of the vinyl esters represented by the formula (III), but preferably used are those having a large solubility of the alkali and being capable of swelling or dissolving the vinyl alcohol polymers formed. Examples of such solvents are cyclic ethers such as tetrahydrofuran and dioxane; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and pinacolin; sulfoxides such as dimethyl sulfoxide; hydrocarbons such as toluene, benzene, n-hexane and cyclohexane; and alcohols such as methanol, ethanol, isopropyl alcohol, n-propyl alcohol, n-butanol, isobutanol, sec-butanol, t-butanol, amyl alcohol and cyclohexanol. These solvents are utilized singly or in a mixture. Preferably used are methyl ethyl ketone, tetrahydrofuran, dioxane, t-butanol and methanol. These solvents can contain a small quantity of water.

The substantial absence of oxygen in the hydrolysis can be generally realized by introducing into the reaction mixture and bubbling therein an inert gas such as nitrogen gas or argon gas which has been deoxygenated. However, since there is no limitation concerning the deoxygenation method in the production processes of the present invention, the substantial absence of oxygen in the reaction mixture can also be realized by incorporating therein an oxygen adsorbent that will not exert harmful influences upon the system. In the hydrolysis, the concentration of dissolved oxygen in the reaction mixture containing the polymer in the form of a polymer solution, a polymer swelled with a solvent or a polymer dispersion is preferably not more than 5×10^{-4} mole/l determined according to Winkler's method. If the hydrolysis is performed in the substantial presence of oxygen, the degree of polymerization of the homopolymers or copolymers of the vinyl esters decreases significantly unless an antioxidant is incorporated into the reaction mixture, and hence vinyl alcohol polymers having a high degree of hydrolysis and a high degree of polymerization are difficult to be obtained.

Any antioxidant may be used in the processes of the present invention insofar as it does not ex rt harmful influences upon the hydrolysis and does not lose its antioxidant activity. Examples of such antioxidants are hindered phenol derivatives such as the compound represented by the following formula (IRGANOX 1010, commercially available from Nippon Ciba-Geigy):



and the compound represented by the following formula (IRGANOX 1098, commercially available from Nippon Ciba-Geigy):



and phenol antioxidants such as hydroquinone and hindered amine antioxidants such as SANOL LS-770 (commercially available from Nippon Ciba-Geigy). These antioxidants can be used singly or in a mixture of two or more. The incorporation of an antioxidant, without any special deoxygenating operation, does not decrease the degree of polymerization of the homopolymers or copolymers of the vinyl esters during the hydrolysis. In case that an antioxidant is employed, a smaller amount of the antioxidant is sufficient if a part of the oxygen would be removed from the system by the above-mentioned processes.

The concentration of the polymers such as the homopolymers or copolymers of the vinyl esters represented by the formula (III) and the vinyl alcohol polymers derived therefrom in the reaction mixture of the hydrolysis can be appropriately selected, depending upon the degree of polymerization of the above polymers.

Generally it ranges between 1 wt% and 70 wt%. The amount of an alkali to be added to the reaction system is represented by the molar ratio of the alkali units to the total vinyl ester units which is inclusive of the vinyl ester units represented by the formula (II) originating from the vinyl ester represented by the formula (III) and the vinyl ester units, used occasionally as a comonomer, originating from a vinyl ester except the vinyl ester represented by the formula (III). The ratio is generally set up in the range between 0.005 and 10. These upper and lower limits are variable, depending upon the desired degree of hydrolysis and the types of solvent and alkali to be utilized. In general, if the ratio is less than 0.005, the degree of hydrolysis does not significantly increase. On the other hand, ratios exceeding 10 accelerate the hydrolysis without any trouble but easily cause the degree of polymerization to decrease. The amount of the alkali used is selected to compensate the consumed amount of alkali in case that the copolymers of the vinyl esters represented by the formula (III) contain a group capable of reacting with the alkali, e.g., a carboxyl group in the monomer units except the total vinyl ester units and in another case that the antioxidant reacts with the alkali. The temperature of the hydrolysis is generally set up in the range between 20 °C and 150 °C. At a higher temperature exceeding 150 °C, the degree of polymerization readily decreases. The time of the hydrolysis is appropriately selected, depending upon the desired degree of hydrolysis, the solvent and alkali employed in the hydrolysis, the molar ratio of the alkali to the total vinyl ester units, and the reaction temperature. After the completion of the hydrolysis, it is preferred that the remaining alkali is neutralized with an acid. Examples of the acids are inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid and carbonic acid or organic acids such as formic acid, acetic acid and benzoic acid, among which organic acids are preferred. The most preferred organic acid is acetic acid. In case that the remaining alkali is not neutralized just after the completion of the hydrolysis, the degree of polymerization of the thus-obtained vinyl alcohol polymers decreases, which is not preferred. Furthermore, unnecessary heating after the completion of the hydrolysis causes the polymer to color yellow or dark brown and decreases the degree of polymerization, which is to be averted.

The vinyl alcohol polymers thus obtained are then purified by conventional methods, for example,by the neutralization of the remaining alkali and the subsequent washing.

As explained in detail heretofore, according to the present invention, there can be easily produced vinyl alcohol polymers having a high syndiotacticity and a high degree of polymerization.

The vinyl alcohol polymers of the present invention are characterized by their high syndiotacticity and a low degree of branching, namely, high linearity.

According to another embodiment of the present invention, introduction of 1,2-glycol units into a highly syndiotactic vinyl alcohol polymer contributes, while disturbing the crystallization of the polymer, to the formation of intermolecular hydrogen bonds in the amorphous region thereof, which cannot be realized by copolymerization methods or partial hydrolysis methods. As a result, in addition to the above-described high syndiotacticity, the polymers will acquire good processability and hence are useable not only in the known fields of polyvinyl alcohols but also in such fields where highly syndiotactic polyvinyl alcohols are demanded but the polym rs ar difficult to apply due to their poor proc ssability.

Application Examples of the vinyl alcohol polymers of the present invention are water-resistant films, heat-resistant films, materials for high-strength gel, paper-processing agents and th like. Thus the vinyl alcohol polymers are highly valuable in the industrial fields. Hereinafter concrete applications the above

polymers are described in detail.

FILMS

Since polyvinyl alcohol films are excellent in mechanical properties, transparency, oxygen-barrier properties, electrical insulating properties at low temperatures, oil resistance and the like, they are utilized in form of films, membranes and sheets as packaging materials for fibrous products, gas barrier materials, membrane filters of various types, separating membranes, electrical insulating materials, optical films such as base materials for light-polarizing films and materials for oil-resistant belts.

However, in recent years, the maintenance of performance in the above-described uses under severer conditions than ever, particularly under high temperatures and high humidities has been required. As a result, at present a film made from a conventional polyvinyl alcohol, which is inferior in water resistance and heat resistance, particularly when having absorbed moisture, cannot cope with the above requirement.

In these circumstances, the present invention provides films comprising novel vinyl alcohol polymers not only having characteristics of conventional polyvinyl alcohols such as high strength, transparency and oil resistance but also being excellent in heat resistance, water resistance and wet heat resistance.

The above films comprise vinyl alcohol polymershaving a syndiotacticity of not less than 55 mol% and a vinyl pivalate units.

Polyvinyl alcohols employed for conventional polyvinyl alcohol films are stereochemically "atactic", and have a syndiotacticity of about 53 mol%. On the other hand, the vinyl alcohol polymer films of the present invention comprise vinyl alcohol polymers having a syndiotacticity of not less than 55 mol% which are hydrolyzed products of the homopolymers or copolymers of vinyl pivalate. Therefore, the above films are characterized by their high strength and water resistance which are considered to originate from the improved crystallinity derived from their high syndiotacticity and from the hydrophobic vinyl pivalate unit.

Hereinafter, the films of the present invention are described in more detail.

The vinyl alcohol polymers forming the films of the present invention have a syndiotacticity of not less than 55 mol%. The increase in syndiotacticity results in an improvement of strength, water resistance and heat resistance, and hence for the purpose of achieving the effect of the present invention it is necessary that the above polymers have a syndiotacticity of not less than 55 mol%, preferably not less than 57 mol%. Since a too high syndiotacticity will cause some troubles during the film-forming step and some difficulties in the production of the above vinyl alcohol polymers, it is preferred that the syndiotacticity be not more than 70 mol%.

The degree of hydrolysis of the vinyl alcohol polymers is not less than 10 mol%, preferably not less than 60 mol%, and in case that heat resistance, water resistance and oil resistance are particularly required, the degree of hydrolysis is preferably 90 to 99.99 mol%. In this case, the degree of hydrolysis represents the ratio of the vinyl alcohol units after the completion of the hydrolysis to the units capable of being changed to vinyl alcohol units by the hydrolysis of the homopolymer or copolymer of vinyl pivalate, and hence the residual group is vinyl pivalate unit.

The intrinsic viscosity of the vinyl alcohol polymers influence the performance of the films of the present invention. The intrinsic viscosity to be achieved is selected appropriately in view of the use of th films obtained. Judging from the film strength and the processing characteristics, it is not less than 0.40 dl/g, preferably not less than 0.70 dl/g, more preferably not less than 1.00 dl/g. Furthermore, it is preferably not more than 5.00 dl/g judging from the processability of the polymers obtained such as film formation and drawing.

The films comprising vinyl alcohol polymers of the present invention have no particular restrictions as to the thickness, shape and transparency, and are generically named as "film", "membrane" or "sheet".

There is also no further particular limitation concerning the process for producing vinyl alcohol polymer films from the above-described vinyl alcohol polymers in the present invention, and the process is appropriately selected in view of the required thickness, uses and objects of the films. Generally mentioned is the film formation from a polymer solution by a casting process, dry process which comprises extruding into air or an inert gas such as nitrogen, wet process which comprises extruding the vinyl alcohol polymers into a poor solvent, dry wet process, and the like. Examples of the solvent used singly or in a mixture are dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, thylene glycol, glycerin, water, hexafluoro isopropanol and the like. Aqueous solutions of inorganic salts such as lithium chloride and calcium chloride can also be used singly or in mixtures with the above-described organic solvents. Preferred solvents are water, dim thyl sulfoxide, a mixture of dimethyl sulfoxide and water, glycerin and ethylene glycol. The concentration of the vinyl alcohol polymers at the time of forming a film is generally from 1 to 50 wt%,

depending upon the process employed.

The temperature of formation is generally in the range of from room temperature to 250° C.

The vinyl alcohol polymer films of the present invention may contain other compounds as long as they do not injure the objects of the present invention. Examples of such compounds are conventional polyvinyl alcohols or other polymers, plasticizers such as glycerin, inorganic compounds such as clay, silica and calcium carbonate, and the like. Furthermore, dyestuffs or pigments for coloring and stabilizers such as antioxidants and ultraviolet absorbents can be optionally incorporated into the above films.

In particular, the films formed from the vinyl alcohol polymer of the present invention are superior in strength, water resistance and heat resistance compared with those formed from conventional polyvinyl alcohols. This fact was achieved for the first time by using vinyl alcohol polymers having a syndiotacticity of not less than 55 mol% which are the hydrolyzed products of the homopolymers or copolymers of vinyl pivalate.

With the best use of the above characteristics, the vinyl alcohol polymer films obtained in the present invention are used as various sorts of packaging materials, gas barrier materials, optical films such as base materials for light-polarizing films and for filters, and various sorts of separation membranes, and are thus of a high industrial value.

GELS

Gels, particularly polymers containing water as a swelling component are known and have found their application in daily lives of mankind. Most of all, various natural gels were at first used in foodstuffs.

Then there have been developed highly water-absorbing gels such as those used for diapers and sanitary napkins, gels for immobilizing enzymes and biomasses, gels having an affinity for living bodies such as contact lenses, artificial muscles and artificial organs, and the like.

Developments in fundamental science on gels represented by the discovery of phase transition phenomenon in gels suggest the possibilities of functional gels as one of advanced techniques, such as sensors, functional separating membranes, release-controlling films, switches, and actuators.

Polymers as base materials for gels are classified into two groups: one group comprises natural polymers such as gelatin and various saccharides; and the other one comprises synthetic polymers such as polyacrylic acid, 2-hydroxyethyl polymethacrylate and polyvinyl alcohols.

In these days, in many cases, new uses of gels often demand high strength, high water resistance, high heat resistance and high durability. Therefore, development of new base materials for gels which can meet the above-mentioned requirements is strongly desired.

In these circumstances, the present invention provides gels with excellent water resistance, heat resistance, durability, and strengh.

The above gels comprise vinyl alcohol polymers having a syndiotacticity of not less than 55 mol%.

Vinyl alcohol polymers have been used as gels in view of their high strength. Conventional polyvinyl alcohols are known as stereochemically "atactic" and have a syndiotacticity of about 53 mol%. The gels of the present invention comprise vinyl alcohol polymers having a syndiotacticity of not less than 55 mol%. The gels comprising the above polymers have a higher syndiotacticity than that of the gels comprising conventional polyvinyl alcohols. Then, the gels comprising the vinyl alcohol polymers of the present invention are characterized by their high water resistance, high heat resistance, high durability, and high strength.

Hereinafter, the present invention is described in more detail.

For the purpose of producing the above-mentioned effects by the increase of syndiotacticity, it is necessary that the polymers have a syndiotacticity of not less than 55 mol%, preferably not less than 57 mol%. With increasing syndiotacticity of the vinyl alcohol polymers, the polymer will be improved in their strength, melting point, water resistance, and heat resistance. Since a too high syndiotacticity will cause some troubles during the gel-producing step and also some difficulties in the production of the vinyl alcohol polymers, it is pref rr d that the syndiotacticity be not more than 75 mol%.

The intrinsic viscosity and the degree of hydrolysis of the vinyl alcohol polym rs also influence the performance of the g ls obtained. The intrinsic viscosity is not less than 0.30 dl/g, preferably not l ss than 1.00 dl/g with a view to a superior strength and processability of th gels. With a view to the processability, it is preferably not m re than 8.00 dl/g. The degree of hydrolysis is not l ss than 70 mol%, preferably not less than 80 mol%.

The gels as ref rred to in the present invention comprise polymers containing water or organic solv nts, which are crosslinked ch mically or physically.

Preferred organic solvents are dimethyl sulfoxide, dimethylformamide, dimethylacetoamide, glycerin, ethylene glycol, and diethylene glycol. The gels of the present invention are prepared according to various processes as mentioned below: a process which comprises first forming vinyl alcohol polymers into sheets or spheres, and then crosslinking the vinyl alcohol polymers by radiation or with a peroxide; a process which comprises gelling by freezing a solution of the polymers or the polymers swelled with a solvent, including repeated freezing and melting; a process which comprises producing granules of precursors of the vinyl alcohol polymers of the present invention such as polyvinyl pivalate by suspension polymerization or precipitation polymerization and then hydrolyzing the precursor, and the like.

The gels of the present invention can be used singly, or in a mixture with other polymers such as a conventional polyvinyl alcohols within the extent of not to impair the purpose of the present invention.

According to the present invention, gels can be obtained which are superior in strength, water resistance and heat resistance compared with gels made from conventional polyvinyl alcohols. Furthermore, the gels of the present invention are extremely useful as base materials for high-solvent-content gels. This was achieved for the first time by using vinyl alcohol polymers having a syndiotacticity of not less than 55 mol%.

With the best use of the above-described characteristics, gels obtained according to the present invention are used for immobilizing enzymes and biomasses, for gels having an affinity for living bodies, such as contact lenses, artificial muscles and artificial organs, functional gels such as sensors, functional separating membranes, release-controlling films, switches, and actuators, and the like.

PROCESS FOR PRODUCING SHAPED ARTICLE

Shaped articles such as films have been formed according to a dry coagulation process, a wet coagulation process, a dry wet coagulation process or a gel coagulation process. These formation processes are appropriately selected in view of the uses and objects of the obtained shaped articles. Among the above there have been preferably employed highly productive wet cogulation process, dry wet coagulation process and gel coagulation process.

Conventional polyvinyl alcohols are atactic and have a syndiotacticity of about 53 mol%. Therefore, in case that these polyvinyl alcohols are formed into shaped articles by wet coagulation or dry wet coagulation, the solutions of the polyvinyl alcohols must be extruded into organic solvents, aqueous solutions of inorganic salts or aqueous solutions of inorganic bases. However, a process which comprises using an organic solvent as coagulation solvent is expensive and entails a fire hazard. Furthermore, a process which comprises using an aqueous solution of inorganic salts or inorganic bases has various problems such as difficulties in operability, corrosion of apparatuses used, poor heat resistance and poor durability, and coloring of obtained shaped articles caused by remaining inorganic salts or inorganic bases.

In these circumstances, the object of the present invention is to provide a process for producing, from vinyl alcohol polymers having a high syndiotacticity, shaped articles having excellent heat resistance and durability, at low costs and with high safety without any problems such as low operability and corrosion of apparatuses.

The above process for producing shaped articles comprises contacting a solution comprising vinyl alcohol polymers having a syndiotacticity of not less than 55 mol% with an aqueous solution containing less than 50 wt% of an organic solvent or with water.

Hereinafter, the present invention is described in more detail.

The vinyl alcohol polymers of the present invention have a syndiotacticity of not less than 55 mol%. With increasing syndiotacticity, the strength, water resistance and heat resistance of the shaped article obtained is improved. For the purpose of producing the effect of the present invention, it is necessary that the vinyl alcohol polymers have a syndiotacticity of not less than 55 mol%, preferably not less than 57 mol%, more preferably not less than 60 mol%.

The degree of hydrolysis of the vinyl alcohol polymers of the present invention is not particularly limited and selected from the range between 10 and 99.99 mol%. In particular, in case that the shaped articles obtained are r quired to be excellent in heat resistance, water resistance and oil r sistanc , the degre of hydrolysis is preferably 70 to 99.99 mol%. The degree of hydrolysis of vinyl alcohol polym rs herein means the ratio of the vinyl alcohol units after the completion of the hydrolysis r action to the units capable of being changed to vinyl alcohol units by the hydrolysis reaction.

The intrinsic viscosity of the vinyl alcohol polymers is not particularly limited and selected appropriately in view of the uses of the shaped articles obtained. With a view to their processability, it is preferably in the range between 0.40 and 15.0 dl/g.

Any solvent can be used for dissolving the vinyl alcohol polymers of the present invention as long as it is capable of dissolving the vinyl alcohol polymers and mixing with water in the coagulation bath. Examples of such solvents are dimethyl sulfoxide, dimethylformamide, dimethylacetamide, ethylene glycol, glycerin, water, hexafluoroisopropanol. These solvents are used singly or in a mixture. Aqueous solutions of inorganic salts such as lithium chloride and calcium chloride can also be used singly or in mixtures with the above organic solvents. Among the above, water, dimethyl sulfoxide, dimethyl sulfoxide with mixed water, glycerin, ethylene glycol, and the like are preferably used. The concentration of the solution at the time of forming a shaped article is generally from 1 to 50 wt% and the temperature at that time is in the range between room temperature and 250 °C.

The process for producing shaped articles according to the present invention comprises subjecting a solution comprising the above vinyl alcohol polymers to coagulation, extraction or the like by contacting with an aqueous solution containing less than 50 wt% of an organic solvent or with a coagulation liquid comprising water. The contact of the above solution with the coagulation liquid is conducted in one or more coagulation baths or extraction baths.

The coagulation bath used in the present invention is composed of water only or an aqueous solution comprising both an organic solvent capable of coagulating the polyvinyl alcohol polymers and water. The aqueous solution contains an organic solvent in an amount of less than 50 wt%. The upper limit of the content of the organic solvent is appropriately selected depending upon the process of coagulation or extraction employed, and, in case that a plurality of coagulation or extraction baths are used, the upper limit can appropriately be selected for each of the coagulation and extraction baths. In case that a wet coagulation process such as a wet film-formation process, or a dry wet coagulation process such as a dry wet film-formation is employed, the content of an organic solvent in the coagulation liquid is preferably less than 30 wt%, more preferably less than 10 wt% for the purpose of achieving rapid coagulation by solvent extraction of a vinyl alcohol polymer solution.

Namely, it is preferred that the coagulation bath comprise water only or an aqueous solution containing an organic solvent in an amount as low as possible. In the process for producing shaped articles of the present invention, it is unnecessary that coagulation baths comprise inorganic salts or inorganic bases, and, in view of the heat resistance or coloring, it is preferred that the baths do not contain such inorganic compounds.

The temperature of the coagulation bath used in the process for producing shaped articles according to the present invention is not particularly limited and selected appropriately depending upon the uses of the shaped articles obtained . The temperature range is between room temperature and the boiling point under atmospheric pressure. However, the temperature range can be selected from a wider range of from the melting point of water to room temperature, and even to the temperature above the boiling point under atmospheric pressure where an autoclave is used. This selection serves the purpose of controlling the speed of the coagulation caused by the extraction of solvent from the solution comprising the vinyl alcohol polymer in case that wet coagulation or dry wet coagulation is employed, or the purpose of controlling the coagulation speed in case that gel coagulation is employed.

The shaped articles obtained by the process of the present invention can be formed into any shape such as films, sheets or the like, which can also be obtained by wet film formation, dry wet film formation or gel film formation, or the like. And further, they can be formed into a shape of a ultrathin film or the like, making the best use of the high water resistance of the vinyl alcohol polymer having a high syndiotacticity.

The shaped articles comprising the vinyl alcohol polymers of the present invention may further contain other compounds as long as they do not injure the objects of the present invention. Examples of such compounds are conventional polyvinyl alcohols or other polymers, platicizers such as glycerin, inorganic compounds such as clay, silica and calcium carbonate, and the like. Furthermore, dyestuffs or pigments for coloring and stabilizers such as antioxidants and ultraviolet absorbers may also be optionally added.

The process for producing shaped articles of the vinyl alcohol polymers of the present invention was completed for the first time by using vinyl alcohol polymers having a syndiotacticity of not less than 55 mol%. The above process can be applied to the production of not only film but also articles having any shape. Furthermore, th process not only provides shaped articles having a higher heat resistance and a higher durability compared with those obtained by conventional production processes but also reduces production costs and involves improvem nts in safety of the process, and is thus of a high industrial value.

Hereinaft r the present invention is described in more detail with r fer nce to the following Examples, which are not intended to be limiting thereof. In the Examples, unless otherwis specified, "part(s)" and "%" are "part(s) by weight" and "% by weight", respectively.

Synthetic Example 1 of Polyvinyl Ester

A Pyrex-glass Kjeldahl flask equipped with a Teflon rotator was charged with 5 ml of vinyl pivalate, 10 ml of distilled water, and 0.5 ml of an emulsifier (an aqueous solution of a sulfonated polyethylene glycol ether represented by

$$C_9H_{19}-\langle\bigcirc\rangle-O(CH_2CH_2O)_m SO_3Na$$

wherein m has a mean value of 18; the content is 65%). The flask, with the mixture, was degassed by repeated freezing and melting, and sealed under a reduced pressure. In a bath of constant temperature at 0° C, the mixture was subjected to polymerization while stirring by irradiation with a 150 W high pressure mercury lamp for 10 hours. After the completion of polymerization, the reaction mixture was poured into a large amount of methanol to recover the obtained polymer. The polymer was then purified by reprecitation using methyl ethyl ketone and water, and dried at 60° C under a reduced pressure to give a homopolymer of vinyl pivalate. The conversion of monomer to polymer was 55.5%.

Synthetic Example 2 of Polyvinyl Ester

Synthetic Example 1 was repeated except for using 3 ml of vinyl pivalate and 2 ml of vinyl acetate instead of 5 ml of vinyl pivalate to obtain a copolymer of vinyl pivalate and vinyl acetate. The conversion of monomer to polymer was 65%.

Examples 1 through 7

A 300-ml reaction vessel equipped with a dropping funnel, reflux condenser, and inlet tube of nitrogen was charged with 2 g of the homopolymer obtained in Synthetic Example 1 or the copolymer obtained in Synthetic Example 2. To the polymer 200 ml of a hydrolysis solvent was added and the mixture was dissolved to give a solution, which was deoxygenated by bubbling a nitrogen gas having a purity of 99.9%. Separately, an alkali was dissolved or dispersed in methanol to a concentration of 25 wt% and the mixture thus formed was deoxygenated by bubbling a nitrogen gas having a purity of 99.9%. The dissolved oxyg n concentration in the polymer solution and that in the mixture of the alkali and methanol thus obtained were measured according to Winkler's method to give a value of not more than 3×10^{-5} mole/l, respectively. After the above mixture of the alkali and methanol had been charged in the above-described dropping funnel, the inner temperature of the reaction system was raised to the hydrolysis temperature described in Table 1.

Then the polymer solution was subjected to hydrolysis by dropwise addition of the above mixture of the alkali and methanol from the dropping funnel in a nitrogen atmosphere for the time described in Table 1. The reaction was terminated by cooling with ice and neutralized with acetic acid. After the completion of the reaction, the product thus obtained was filtered, washed thoroughly with methanol, and dried at 60° C und r a reduced pressure. The hydrolysis conditions employed and the colors and analytical results of the vinyl alcohol polymers obtained are summarized in Table 1. The 400MHz ^{1}H-NMR spectrum, measured in d_6-DMSO using a Model GX-400 NMR spectrometer available from JEOL Ltd., of the vinyl alcohol polymer obtained in Example 1 is shown in Figure 1.

Example 8

The same procedures as in Examples 1 through 7 w re followed except that bubbling with nitrogen in the polymer solution and in the mixture of an alkali and methanol was not conducted, that 0.01 g of an antioxidant (IRGANOX 1010 available from Nippon Ciba-Geigy) was used, and that the atmosphere of hydrolysis was changed to air.

The hydrolysis conditions employed and the color and analytical results of the vinyl alcohol polymer obtained are shown in Table 1.

Comparative Example 1

The same procedures as in Examples 1 through 7 were followed except that bubbling with nitrogen in the polymer solution and in the mixture of an alkali and methanol was not conducted and that the atmosphere of hydrolysis reaction was changed to air. The hydrolysis conditions employed and the color and analytical results of the vinyl alcohol polymer obtained are shown in Table 1. The dissolved oxygen concentration of the polymer solution and that in the mixture of the alkali and methanol were more than 1.6 $\times 10^{-3}$ mole/l, respectively.

Table 1-1

	Hydrolysis conditions					
	Solvent	Polymer*1	Alkali		Temperature (°C)	Time (hr)
			Compound	Molar ratio*2		
Example 1	tetrahydrofuran	[A]	KOH	6.0	40	0.83
〃 2	tetrahydrofuran	[A]	KOH	6.0	60	0.25
〃 3	tetrahydrofuran	[A]	NaOH	6.0	60	0.5
〃 4	acetone	[A]	KOH	6.0	reflux	0.17
〃 5	dioxane	[A]	KOH	2.0	60	2.0
〃 6	tetrahydrofuran	[B]	KOH	6.0	60	0.25
〃 7	tetrahydrofuran	[B]	KOH	6.0	60	0.10
〃 8	acetone	[A]	KOH	6.0	60	0.50
Comparative Example 1	acetone	[A]	KOH	6.0	reflux	72

(Not s) *1: [A]: the polymer used was the homopolymer of vinyl pivalate obtained in Synthetic Example 1

[B]: the polymer used was the copolymer of vinyl pivalate and vinyl acetate obtained in Synthetic Example 2.

*2: Molar ratio represents the molar ratio of an alkali to total vinyl ester units.

Table 1-2

	Polyvinyl alcohol polymers				
	Color	Analytical results			
		Composition (mol%) *3		[η] *4	Syndiotacticity *5
		(1)	(2)	(dl/g)	(mol%)
Example 1	no	98.8	1.2	4.13	63
〃 2	no	98.5	1.5	3.66	63
〃 3	no	83.0	17.0	2.94	--
〃 4	no	94.0	6.0	2.93	61
〃 5	no	98.7	1.3	2.85	63
〃 6	no	99.0	1.0	2.48	57
〃 7	no	78.0 *6	20.0 *6	2.52	--
〃 8	light gray	99.0	1.0	2.90	63
Comparative Example 1	dark brown	99.0	1.0	0.59	--

(Notes) *3: The composition ratio determined according to the 400 MHz ^{1}H-NMR spectrum measured in d_6-DMSO using a Model GX-400 available from JEOL Ltd., wherein (1) shows the mol% of vinyl alcohol units represented by the formula (I) in total monomer units and (2) shows the mol% of vinyl ester units represented by the formula (II) wherein each of R^1, R^2 and R^3 is a methyl group in total units. The NMR spectrum of the vinyl alcohol polymer obtained from the polymer of Example 1 dissolved in d_6-DMSO is shown in Figure 1.

*4: The intrinsic viscosity of a polyvinyl acetate polymer obtained by acetylation measured in benzene at 30°C.

*5: The diad syndiotacticity determined according to the 400 MHz ^{1}H-NMR spectrum measured in d_6-DMSO using a Model GX-400 available from JEOL Ltd.

*6: The residual composition other than (1) and (2) (2 mol%) is vinyl acetate.

Example 9

An autoclave quipped with a stirrer was charged with 90 parts of vinyl pivalate monomer, and deoxygenated with nitrogen by repeated application of pr ssure and discharge. 0.000277 Part of 2,2-azobis-

(2,2,4-trimethylpentane) (VR-110 available from Wako Pure Chemical Industries, Ltd.) as initiator was dissolved in 10 parts of vinyl pivalate monomers. After the solution thus obtained had been thoroughly deoxygenated by bubbling with nitrogen, the autoclave with its content was heated. When the inner temperature reached 120° C, the monomers were subjected to polymerization by adding the solution containing the initiator. After 2 hours, the reaction was terminated by cooling. The content of the autoclave was added to a large amount of methanol to recover the polymer obtained. The polymer was purified twice by reprecipitation using acetone and methanol, and dried at 60° C under a reduced pressure. The polymer obtained weighed 8.2 parts.

Next, 1 part of the thus-obtained polymer was dissolved in 49 parts of tetrahydrofuran deoxygenated with nitrogen and the solution obtained was maintained at 60° C. To this solution 10.5 parts of a 25% potassium hydroxide solution in methanol which had separately been prepared and deoxygenated with nitrogen were added, and the resulting mixture was stirred thoroughly. At this time, the dissolved oxygen concentrations of both the polymer solution and the potassium hydroxide solution determined according to Winkler's method were not more than 3×10^{-5} mole/l. The solution gelled in 5 minutes after the completion of the addition of the 25% potassium hydroxide solution, and was maintained at 60° C for additional 25 minutes. Thereafter, the potassium hydroxide was neutralized by adding 3.4 parts of acetic acid and 10.1 parts of methanol. The gel thus formed was pulverized and cleaned with methanol using a Soxhlet extractor to give a vinyl alcohol polymer.

A mixture of 0.1 part of the vinyl alcohol polymer thus obtained, 10 parts of acetic anhydride and 2 parts of pyridine was sealed in a tube, and the vinyl alcohol polymer was acetylated by heating at 120° C for 3 hours. The polyvinyl acetate obtained was precipitated in n-hexane and purified twice by re-precipitation using acetone and n-hexane.

The NMR spectrum of the thus-obtained polyvinyl alcohol dissolved in d_6-DMSO showed that it had a degree of hydrolysis of 99.6 mol%, a syndiotacticity of 60.2 mol%, and a content of 1,2-glycol units of 2.29 mol%. The polyvinyl acetate obtained above by acetylating the vinyl alcohol polymer had an intrinsic viscosity, measured in benzene at 30° C, of 3.65 dl/g.

Example 10

An autoclave equipped with a stirrer was charged with 90 parts of vinyl pivalate monomer and 0.86 part of vinylene carbonate, and was deoxygenated with nitrogen by repeated application of pressure and discharge. 0.00827 Part of 2,2′- azobis-4-methoxy-2,4-dimethylvaleronitrile as initiator was dissolved 10 to parts of vinyl pivalate monomers. The solution thus obtained was thoroughly deoxygenated by bubbling with nitrogen.

The autoclave with its content was heated. When the inner temperature reached 30° C, the monomers were subjected to polymerization by adding the solution containing the initiator.

After 3 hours, the reaction was terminated by cooling, and the content of the autoclave was poured into a large amount of methanol to recover the polymer obtained. The polymer was purified twice by the reprecipitation using acetone and methanol, and dried at 60° C under a reduced pressure. The polymer weighed 9.5 parts.

Next, 1 part of the thus-obtained polymer was dissolved in 49 parts of tetrahydrofuran deoxygenated with nitrogen, and the solution obtained was maintained at 60° C. Then, to this solution 10.5 parts of a 25% potassium hydroxide solution in methanol which had been prepared and deoxygenated with nitrogen were added, and the resulting mixture was stirred thoroughly. At this time, the dissolved oxygen concentrations of both the polymer solution and the potassium hydroxide solution determined according to Winkler's method were not more than 3×10^{-5} mole/l. The solution gelled in 5 minutes after the completion of the addition of the 25% potassium solution, and was maintained at 60° C for additional 25 minutes. Thereafter, the potassium hydroxide was neutralized by adding 3.4 parts of acetic acid and 10.1 parts of methanol. The gel thus formed was pulverized and cleaned with methanol using a Soxhlet extractor to give a vinyl alcohol polymer.

A mixture of 0.1 part of the vinyl alcohol polymer thus obtained, 10 parts of acetic anhydride, and 2 parts of pyridine was sealed in a tube, and the vinyl alcohol polymer was acetylated by heating at 120° C for 10 hours. The polyvinyl acetate obtained was precipitated in n-hexane and purified twice by re-precipitation using acetone and n-hexane.

The NMR spectrum of the thus-obtained vinyl alcohol polymer dissolved in d_6-DMSO showed that it had a degree of hydrolysis of 99.6 mol%, a syndiotacticity of 60.2 mol%, and a content of 1,2-glycol units of 2.5 mol%. The polyvinyl acetate obtained above by acetylating the vinyl alcohol had an intrinsic

viscosity, measured in benzene at 30°C, of 4.15 dl/g.

The vinyl alcohol polymers her tofore obtained in Examples 1, 9, and 10 were evaluated for their solubilities in water and DMSO. The results are summarized in Table 2.

Table 2

	Water		DMSO	
	90°C	110°C	25°C	80°C
Polyvinyl alcohol of Example 9	x – Δ (4 hours)	O (4 hours)	O (12 hours)	O (6 hours)
Polyvinyl alcohol of Example 10	x – Δ (4 hours)	O (4 hours)	O (12 hours)	O (6 hours)
Polyvinyl alcohol of Example 1	x (4 hours)	Δ (4 hours)	x (3 days)	O (3 days)
Solubility ratings: O : soluble, Δ : partly soluble, x : insoluble				

Examples 11 through 13

A reaction vessel equipped with a stirrer was charged with 600 parts of vinyl pivalate monomer and 200 parts of methanol, and was deoxygenated by bubbling with nitrogen. 0.0712 Part of 2,2′-azobisisobutyronitrile as initiator was dissolved in 26 parts of methanol, and the resulting solution was thoroughly deoxygenated by bubbling with nitrogen. The reaction vessel with its content was heated. When the inner temperature reached 60°C, the monomers were subjected to polymerization by adding the solution containing the initiator. After 190 minutes, when the conversion of monomers to polymer reached 50%, the reaction was terminated by cooling, and then the unreacted vinyl pivalate monomers were removed under a reduced pressure, while sometimes t-butanol was being added to obtain a solution of polyvinyl pivalate in t-butanol. The butanol was removed under a reduced pressure to obtain a polyvinyl pivalate.

Next, a reaction vessel equipped with a stirrer and a reflux condenser was charged with 10 parts of polyvinyl pivalate thus obtained, and the inner space of the reaction vessel was replaced with nitrogen by repeated degassing under a reduced pressure and charge with nitrogen. Thereafter, in this reaction vessel 90 parts of a solvent for hydrolysis reaction as shown in Table 3, which had been deoxygenated by bubbling with nitrogen were added, and the resulting mixture was heated with stirring to 60°C to give a solution. To this solution 21 parts of a solution of 25% potassium hydroxide in methanol which had been prepared and deoxygenated with nitrogen were added, and the resulting mixture was thoroughly mixed with stirring. At this time, the dissolved oxygen concentrations of both the polymer solution and the potassium hydroxide solution determined according to Winkler's method were not more than 3×10^{-5} mole/l. The reaction vessel was maintained at 60°C in a nitrogen atmosphere for 2 hours, and then neutralized by adding 6.8 parts of acetic acid and 20 parts of methanol. The gel thus formed was pulverized and cleaned with m thanol using a Soxhlet extractor to give a vinyl alcohol polymer. A mixture of 0.5 part of the polyvinyl alcohol thus obtained, 10 parts of acetic anhydride, and 2 parts of pyridine was sealed in a tube, and the vinyl alcohol polymer was acetylated by heating at 120°C for 8 hours. The polyvinyl acetat obtained was precipitated in n-hexan and purified twice by reprecipitation using acetone and n-hexan .

Th NMR spectrum f th thus-obtained polyvinyl alcohol dissolved in d_6-DMSO was measured to obtain the degree of hydrolysis, syndiotacticity, and the content of 1,2-glycol units. The polyvinyl acetate obtained above by the reacetylation was measured for the intrinsic viscosity in benz ne at 30°C. The syndiotacticity and the content of 1,2-glycol units wer 61.4 mol% and 1.70 mol%, respectiv ly. Th r sults

are shown in Table 3.

Table 3

Example	Hydrolysis solvent	Degree of hydrolysis (mol%)	Intrinsic viscosity (dl/g)
11	methyl ethyl ketone	99.1	1.10
12	tetrahydrofuran	98.9	1.08
13	t-butanol	92.6	1.12

Example 14

A reaction vessel equipped with a stirrer and reflux condenser was charged with 10 parts of the polyvinyl pivalate synthesized in Example 11, and the inner space of the reaction vessel was deoxygenated with nitrogen by repeated degassing under a reduced pressure and charged with nitrogen. Thereafter, to this reaction vessel 90 parts of methyl ethyl ketone which had been deoxygenated with nitrogen were added, and the resulting mixture was heated with stirring to 60°C to give a solution. To this solution 16.1 parts of a 1.1% sodium methylate in methanol which had been prepared and deoxygenated with nitrogen were added, and the resulting mixture was thoroughly mixed with stirring. At this time, the dissolved oxygen concentrations of both the polymer solution and the sodium methylate solution determined according to Winkler's method were not more than 3×10^{-5} mole/l. The reaction vessel was maintained at 60°C in a nitrogen atmosphere for 80 minutes, and then neutralized by adding 0.25 part of acetic acid and 20 parts of methanol. The gel thus formed was pulverized and cleaned with methanol using a Soxhlet extractor to give a vinyl alcohol polymer.

The NMR spectrum of the thus-obtained polyvinyl alcohol dissolved in a mixed solvent comprising d_6-DMSO and $CDCl_3$ showed that it had a degree of hydrolysis of 30.1 mol%.

Example 15

An autoclave equipped with a stirrer was charged with 90 parts of polyvinyl pivalate monomer, and was deoxygenated with nitrogen by repeated application of pressure and discharge. 0.00125 Part of 2,2′-azobisisobutyronitrile as initiator was dissolved in 10 parts of vinyl pivalate monomer. The solution thus obtained was thoroughly deoxygenated by bubbling with nitrogen.

The autoclave with its content was heated. When the inner temperature reached 60°C, the monomers were subjected to polymerization by adding the solution containing the initiator.

After 90 minutes, the reaction was terminated by cooling, and the content of the autoclave was pour d into a large amount of methanol to recover the polymer obtained. The polymer was purified twice by the reprecipitation using acetone and methanol, and dried at 60°C under a reduced pressure. The polymer obtained was 6.5 parts.

Next, 1 part of the thus-obtained polymer was dissolved in 49 parts of tetrahydrofuran deoxygenat d with nitrogen, and the solution obtained was maintained at 60°C. And then, to this solution 10.5 parts of a 25% potassium hydroxide solution in methanol which had been prepared and deoxygenated with nitrog n were added, and the resulting mixture was stirred thoroughly. At this time, the dissolved oxygen concentrations of both the polymer solution and the potassium hydroxide solution determined according to Winkler's m thod wer not more than 3×10^{-5} mole/l. Th hydrolysis solution gelled in about 5 minutes after the compl tion of th addition of the 25% potassium hydroxide solution, and was maintained at 60°C for additional 25 minutes. Thereafter, the potassium hydroxide was neutralized by adding 3.4 parts of acetic acid and 10.1 parts of methanol. The gel thus formed was pulverized and cleaned with methanol using a Soxhl t extractor to give a vinyl alcohol polymer. A mixture of 0.1 part of the vinyl alcohol polymer thus obtain d, 10 parts of acetic anhydrid , and 2 parts of pyridine was sealed in a tube, and the vinyl alcohol polym r was acetylated by heating at 120°C for 3 hours. Th polyvinyl acetat was precipitated in n-

hexane and purified twice by the reprecipitation using acetone and n-hexane.

The NMR spectrum of the thus-obtained vinyl alcohol polymer dissolved in d_6-DMSO showed that it had a degree of hydrolysis of 99.7 mol%, a syndiotacticity of 61.5 mol%, and a content of 1,2-glycol units of 1.70 mol%. The polyvinyl acetate obtained above by acetylating the vinyl alcohol polymer had an intrinsic viscosity, measured in benzene at 30° C, of 6.80 dl/g.

Example 16

A reaction vessel equipped with a stirrer was charged with 100 parts of vinyl pivalate monomer and 0.00827 part of 2,2′-azobisisobutyronitrile, and was deoxygenated by bubbling with nitrogen. Thereafter, the resulting mixture was immediately cooled until the inner temperature of the reaction vessel reached -30° C. Then the reaction mixture was subjected to polymerization while stirring by irradiation from a distance of 15 cm using a Model UM452 high pressure mercury lamp having a rated demand of 450 W available from Ushio Inc. After 70 minutes, the irradiation was terminated, and the content of the reaction vessel was poured into a large amount of methanol to recover the polymer obtained. The polymer was purified twice by the reprecipitation using acetone and methanol, and dried at 60° C under a reduced pressure. The polymer obtained weighed 5.4 parts.

Next, 1 part of the thus-obtained polymer was dissolved in 49 parts of methyl ethyl ketone deoxygenated with nitrogen, and the solution obtained was maintained at 60° C. And then, to this solution 10.5 parts of a 25% methanol solution of potassium hydroxide which had been prepared and deoxygenated with nitrogen were added, and the resulting mixture was stirred thoroughly. At this time, the dissolved oxygen concentrations of both the polymer solution and the potassium hydroxide solution determined according to Winkler's method were not more than 3×10^{-5} mole/l. The solution gelled in about 5 minutes after the completion of the addition of the25% potassium hydroxide solution, and was maintained at 60° C for additional 25 minutes. Thereafter, the potassium hydroxide was neutralized by adding 3.4 parts of acetic acid and 10.1 parts of methanol. The gel thus formed was pulverized and cleaned with ethanol using a Soxhlet extractor to give a vinyl alcohol polymer. A mixture of 0.1 part of the vinyl alcohol polymer thus obtained, 10 parts of acetic anhydride, and 2 parts of pyridine was sealed in a tube, and the vinyl alcohol polymer was acetylated by heating at 120° C for 3 hours. The polyvinyl acetate obtained was precipitated in n-hexane and purified twice by reprecipitation using acetone and n-hexane. The NMR spectrum of the thus-obtained vinyl alcohol polymer dissolved in d_6-DMSO showed that it had a degree of hydrolysis of 99.6 mol%, a syndiotacticity of 64.0 mol%, and a content of 1,2-glycol units of 0.80 mol%. The polyvinyl acetate obtained above by acetylating the vinyl alcohol polymer had an intrinsic viscosity, measured in benzene at 30° C, of 2.95 dl/g.

Example 17

An autoclave equipped with a stirrer was charged with 90 parts of vinyl pivalate monomer, and was deoxygenated with nitrogen by repeated application of pressure and discharge. 0.000091 Part of 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) as initiator was dissolved in 10 parts of vinyl pivalate monomer. The solution thus obtained was thoroughly deoxygenated by bubbling with nitrogen.

The autoclave with its content was heated. When the inner temperature reached 30° C, the monomers were subjected to polymerization by adding the solution containing the initiator.

After 10 hours, the reaction was terminated by cooling, and the content of the autoclave was poured into a large amount of methanol to recover the polymer obtained. The polymer was purified twice by the reprecipitation using acetone and methanol, and dried at 60° C under a reduced pressure. The polymer obtained weighed 4.2 parts.

Next, 1 part of the thus-obtained polymer was dissolved in 49 parts of tetrahydrofuran deoxygenated with nitrogen, and the solution obtained was maintained at 60° C. And then, to this solution 10.5 parts of a 25% potassium hydroxide solution in methanol which had been prepared and deoxygenated with nitrog n were added, and the resulting mixture was stirred thoroughly. At this time, the dissolved oxygen concentrations of both the polymer solution and the potassium hydroxide solution determined according to Winkler's method were not more than 3×10^{-5} mole/l. The solution gelled after about 5 minutes, and was maintained at 60° C for additional 25 minutes. Ther after, the potassium hydroxide was neutralized by adding 3.4 parts of acetic acid and 10.1 parts of methanol. The gel thus formed was pulverized and cl aned with m thanol using a Soxhlet extractor to give a vinyl alcohol polymer. A mixtur of 0.05 part of the vinyl alcohol polym r

thus obtained, 10 parts of acetic anhydride, and 2 parts of pyridine was sealed in a tube, and the vinyl alcohol polymer was acetylated by heating at 120 °C for 3 hours. The polyvinyl acetate was precipitated in n-hexane and purified twice by reprecipitation using acetone and n-hexane.

The NMR spectrum of the thus-obtained vinyl alcohol polymer dissolved in d_6-DMSO showed that it had a degree of hydrolysis of 99.7 mol%, a syndiotacticity of 61.5 mol%, and a content of 1,2-glycol units of 1.42 mol%. The polyvinyl acetate obtained above by reacetylating the vinyl alcohol polymer had an intrinsic viscosity, measured in benzene at 30 °C, of 9.72 dl/g.

Example 18

The vinyl alcohol polymer obtained in Example 11 was dissolved in dimethyl sulfoxide to give a 7 wt% solution, and the resulting solution was spread over a polyethylene terephthalate film and then immersed into a methanol bath to give a film. The film obtained was rinsed thoroughly with methanol, air-dried, and then heat-treated at 160 °C for 10 minutes to give a film having a thickness of 100 µm. The film thus obtained was immersed in boiling water for an hour. It maintained the shape of film, somewhat swelled though.

Comparative Example 2

A polyvinyl alcohol having obtained by hydrolyzing a polyvinyl acetate and having a degree of hydrolysis of 99.9 mol% and a syndiotacticity of 52.8 mol% and the reacetylated product of which had an intrinsic viscosity of 0.89 dl/g was formed in the same manner in Example 18 into a film having a thickness of 100 µm. The film obtained perfectly dissolved in boiling water. As a result, it became clear that the film comprising the vinyl alcohol polymers of the present invention have an excellent water resistance.

Example 19

The vinyl alcohol polymer obtained in Example 11 was dissolved in a mixed solvent of DMSO and water prepared in a weight ratio of 80/20 to give 5 wt% and 2 wt% solutions. These solutions were allowed to stand at -10 °C for 3 hours to give two gels. And immediately thereafter, the gels were transferred to a bath to measure their melting temperatures. The melting temperature was measured by putting a steel ball having a weight of 1.06 g on the upper part of a specimen gel placed in a test tube having an inner diameter of 12.8 mm , heating it at a rate of 0.4 ° to 0.5 °C/min and observing the temperature when the whole ball sank in the gel. The results are shown in Table 4.

Comparative Example 3

Example 19 was repeated except for using a polyvinyl alcohol having an intrinsic viscosity of 1.11 dl/g, a degree of hydrolysis of 99.5 mol% and a syndiotacticity of 53 mol% to obtain a gel and measure the melting temperature thereof. The results are summarized in Table 4.

Table 4

	Concentration of polyvinyl alcohol (wt%)	5	2
Example 19	Melting temperature (°C)	86	72
Comparative Example 3	Melting t mp rature (°C)	62	< 20

As is apparent from the above results, the gels of the present invention have a higher melting temperature and are superior in heat resistance compared with conventional polyvinyl alcohol gels. Furthermore, the gels of the present invention are capable of producing a high-solvent-content gel, which is

one of the characteristics of the present invention.

Example 20

The vinyl alcohol polymer obtained in Example 11 was dissolved in 95 parts of dimethyl sulfoxide to give a solution, and the resulting solution was casted at a temperature of 80 °C over a polyethylene terephthalate film using a bar coater with a spacer having a thickness of 1.0 mm. The film-like shaped article obtained was immersed in sufficient amount of water to coagulate therein for about 30 minutes at room temperature, and the coagulated film was dried for about 60 minutes in a hot circulating air at 40 °C, to give a polyvinyl alcohol film.

The film obtained did not show any change such as discoloring even when the film was allowed to stand in a drying oven at a temperature of 90 °C for 100 hours, and was thus of excellent heat resistance and durability.

Comparative Example 4

Example 20 was repeated except for using a coagulation liquid comprising 300 parts of sodium sulfate and 700 parts of water instead of distilled water to obtain a polyvinyl alcohol film.

The film thus obtained was allowed to stand in a drying oven at a temperature of 90 °C for 100 hours, and as a result it discolored to brown and thus was of inferior heat resistance and durability.

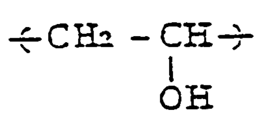
Comparative Example 5

Example 20 was repeated except for using a polyvinyl alcohol obtained by hydrolyzing a polyvinyl acetate having a degree of hydrolysis of 99.9 mol%, a syndiotacticity of 52.8 mol% and an intrinsic viscosity of 0.89 dl/g. A film formation was attempted using the polyvinyl alcohol thus obtained, but the polyvinyl alcohol did not coagulate and remained dissolved.

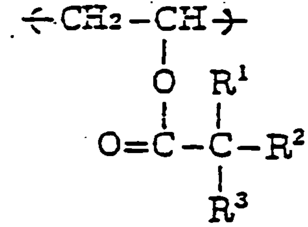
Obviously, numerous modifications and variations of the present invention are possible in the light of the above disclosures. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Claims

1. Vinyl alcohol polymers containing a unit (I) and a unit (II) represented by the following formulae, having a content of the unit (I) from 10 to 99.99 mol% and a content of the unit (II) from 90 to 0.01 mol%, a diad syndiotacticity of not less than 55 mol% and an intrinsic viscosity of polyvinyl acetate obtained by acetylation of 0.7 dl/g, which is measured in benzene at 30 °C.



(I)



(II)

wherein R_1 is a hydrogen atom or a hydrocarbon group, and each f R_2 and R_3 is a hydrocarbon group.

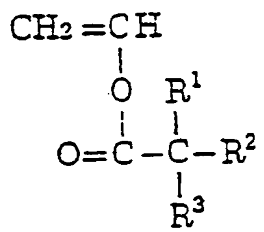
2. The vinyl alcohol polymers according to Claim 1 wherein the content of the unit (I) is from 45 to 99.99 mol% and the content of the unit (II) is from 45 to 0.01 mol%.

3. The vinyl alcohol polymers according to Claim 2 wherein the content of the unit (I) is from 70 to 99.5 mol% and the content of the unit (II) is from 30 to 0.50 mol%.

4. The vinyl alcohol polymers according to Claim 1 wherein the content of the unit (I) is from 10 to 55 mol% and the content of the unit (II) is from 90 to 45 mol%.

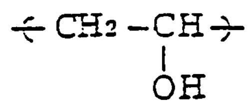
5. The vinyl alcohol polymers according to Claim 1 wherein the unit (II) is a vinyl pivalate unit.

6. process for producing vinyl alcohol polymers which comprises hydrolyzing, in the substantial absence of oxygen or in the presence of an antioxidant, a homopolymer or copolymer of a vinyl ester represented by the following formula:

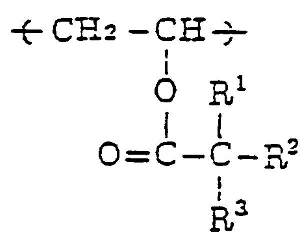


(III)

wherein R_1, R_2 and R_3 are the same as defined in Claim 1 said vinyl alcohol polymers containing units represented by the following formula:



and units represented by the following formula:



wherein R_1, R_2 and R_3 are the same as defined in Claim 1.

7. The process for producing vinyl alcohol polymers defined in Claim 1 according to Claim 6.

8. A film comprising vinyl alcohol polymers having a syndiotacticity of not less than 55 mol% and vinyl pivalate units.

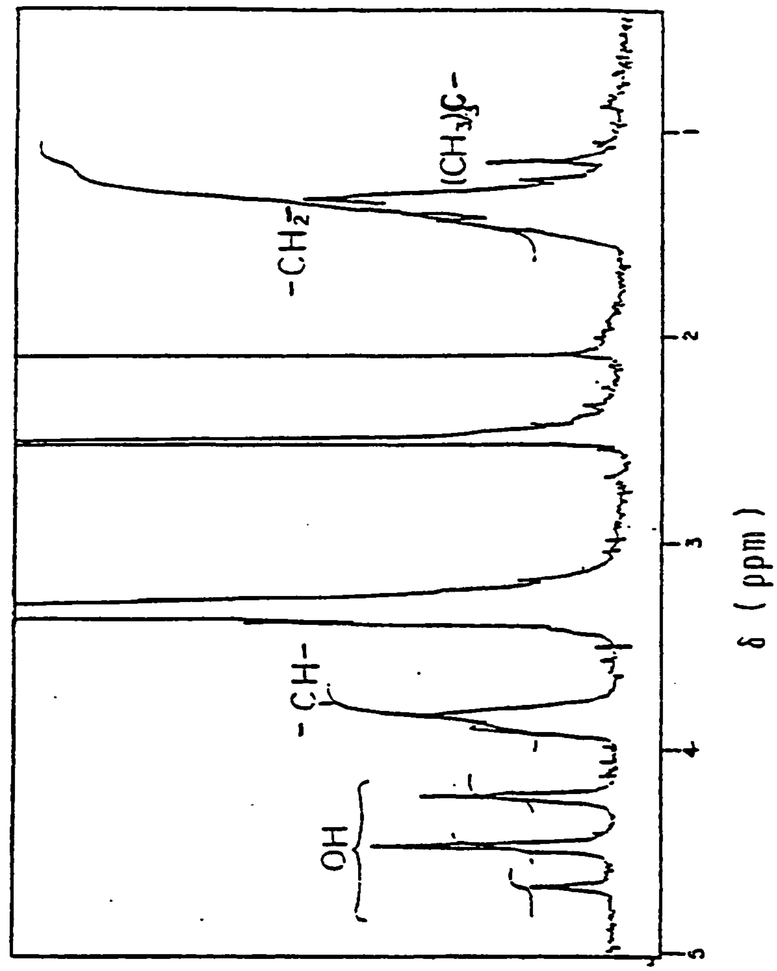
9. The film according to Claim 8 wherein the vinyl alcohol polymers have a degree of hydrolysis of not less than 60 mol% and an intrinsic viscosity of not less than 0.70 dl/g wherein said intrinsic viscosity is the same as defined in Claim 1.

10. A gel comprising vinyl alcohol polymers having a syndiotacticity of not less than 55 mol%.

11. The gel according to Claim 10 wherein the vinyl alcohol polymers have an intrinsic viscosity of not less than 1.0 dl/g wherein said intrinsic viscosity is the same as defined in Claim 1.

12. A process for producing shaped articles comprising vinyl alcohol polymers which comprises contacting a solution comprising vinyl alcohol polymers having a syndiotacticity of not less than 55 mol% with an aqueous solution containing an organic solvent in an amount of less than 50 wt%.

Figure 1



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EUROPEAN SEARCH REPORT

Application Number

EP 90 10 4265

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	JOURNAL OF POLYMER SCIENCE, POLYMER CHEMISTRY EDITION. vol. 26, no. 7, July 1988, NEW YORK US pages 1961 - 1968; K. IMAI: "Poly(vinyl Alcohol) Obtained through Polymerization of Some Vinyl Esters" * page 1963, line 21 - page 1964, line 5 *	1-5	C08F8/12
P,X	PATENT ABSTRACTS OF JAPAN & JP-A-01 319505 (KURARAY KK) 25 December 1989, * the whole document *	1-5	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02 AUGUST 1990	SERRAVALLE M.

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